Reducing Phosphorus in Swine Effluent with Aluminum Chloride Treatment during Lagoon Cleanout

P. B. DeLaune, P. A. Moore, Jr., S. Formica

Abstract. *Phosphorus (P) runoff from agricultural lands fertilized with swine manure can be a significant environmental issue. The objectives of this study were to evaluate the effect of aluminum chloride ($AlCl_3$) applications to a swine lagoon during total clean out on P concentrations in manure and runoff water. There were four treatments: 1) untreated manure; 2) manure treated with $AlCl_3$* in-situ*; 3) manure treated with $AlCl_3$ post collection; and 4) manure treated with $AlCl_3$ plus lime post collection. Manure applications were equivalent to 112 kg P ha^{-1}. Rainfall simulators were used to provide a 5-cm h^{-1} storm event 1, 8, 15, 17, and 24 days after application. All $AlCl_3$ amendments significantly reduced manure soluble reactive P (SRP) concentrations. The $AlCl_3$/lime treatment was the most effective, reducing manure SRP concentrations by 69% compared to the untreated manure. In runoff water, SRP loads were significantly higher from plots fertilized with the untreated manure. Cumulative SRP loads were 30% lower from plots fertilized with manure treated with $AlCl_3$* in-situ *than the untreated manure. Cumulative P losses increased as SRP application rates increased. Treatment of manure with $AlCl_3$* in-situ *can significantly decrease manure SRP concentrations and subsequently reduce P loss from fields receiving manure applications.*

Keywords. *Agricultural runoff, Chemical treatment, Non-point source pollution, Phosphorus, Simulated rainfall, Swine lagoon liquid.*

More stringent environmental regulation, such as a change from N-based to P-based nutrient management planning, has resulted in an increased awareness of the relationship between animal feeding operations and water resources. Due to historical N-based nutrient management and low N:P ratios of animal manures, P can be over-applied and become a major contributor to eutrophication in areas with intensive animal feeding operations. As most states have adopted a P Index, many have restricted manure application compared to years past. Soluble P in manure has been shown to be an important factor regulating P runoff (Kleinman et al., 2002; DeLaune et al., 2004). It is a major component of the Arkansas P Index and the Eucha-Spavinaw P Index, indices implemented in Arkansas and northeast Oklahoma (DeLaune et al., 2004; 2006). Thus, controlling P in the manure prior to land application is a practical process to reduce P runoff.

Manure P can be affected by diet management and manure treatment. Smith et al. (2004) reported that phytase amended diets alone reduced soluble reactive P (SRP) concentrations in swine manure by 17%. Several studies have demonstrated manure amendment technologies that significantly reduce P in manure. Significant reductions in manure P have been noted using Fe, Ca, and Al based products in both wet and dry manure systems (Moore and Miller, 1994; Barrow et al., 1997; Sherman et al., 2000; Smith et al., 2001, 2004; DeLaune et al., 2004, 2006; Timby et al., 2004; Zhu et al., 2004). In wet manure systems, combining these chemical amendments with polymers have been shown to be very effective in flocculating solids and removing P (Timby et al, 2004; Singh et al., 2006; DeBusk et al., 2008). Smith et al. (2004) reported reductions in manure SRP as well as ammonia emissions when $AlCl_3$ was applied within pits of a swine housing facility. Research has indicated that Al-based chemicals are more effective in P removal than Fe- or Ca-based materials due to stability of aluminum phosphates over a wide range of soil physical and chemical conditions (Moore and Miller, 1994; Barrow et al., 1997; Sherman et al., 2000).

As expected, P removal prior to land application can have a substantial impact on P runoff. DeLaune et al. (2004) reported a significant linear relationship between the amount of alum in poultry litter and SRP concentrations in runoff water, with SRP concentrations in runoff significantly decreasing as the alum rate increased. Phosphorus runoff has been shown to be 73% lower from field-scale watersheds fertilized with alum-treated poultry litter receiving natural rainfall compared with those amended with normal poultry litter (Moore et al., 2000). Smith et al. (2001, 2004) found that Al-based amendments to swine manure reduced P runoff by as much as 84%.

Of the few studies that have evaluated manure treatments at a scale larger than lab or bench scale, they have focused on removal systems prior to delivery to a storage facility such as a lagoon. An important component of each liquid waste system is the storage structures typically consisting of earthen ponds. Most waste system ponds are designed for a

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minimum storage capacity of waste water and solids anticipated from the number of animals confined by the facility. Waste is held in storage until it can be land applied as a fertilizer, typically to forage crops. In Arkansas, Van Eps et al. (1998) reported that 52% of sampled holding ponds were determined to have severe solids accumulation problems. An accumulation of nutrients, including soluble P, was also found as a result of solid accumulation. In order to reduce waste system related problems associated with accumulation of solids and the resultant loss of storage capacity, farmers are encouraged to clean out their ponds. The waste from these holding ponds will then be land applied to nearby pastureland. Concerns could result as the sludge is high in nutrients, particularly P, which could lead to water quality degradation. No studies have observed the effect of aluminum chloride treatments to swine lagoon liquid *in-situ*. The objectives of this study were to determine the effect of aluminum chloride on manure P solubility and P runoff from swine manure treated *in-situ* during lagoon cleanout.

Materials and Methods

Swine manure was collected from a lagoon undergoing total cleanout (solids being removed) in central Arkansas. The commercial farm was a sow-pig farrowing facility that used a liquid management system to handle generated waste. Waste material was flushed from the barns to a lagoon, from which solids had not been completely removed in at least 10 years. The lagoon was agitated using a Houle Agisprayer (GEA Houle Inc., Wickman, Quebec, Canada) and allowed to mix for 4 h. At this time, 1893 L of waste was collected as the untreated control sample. Thereafter, 4164 L of liquid $AlCl_3$ (provided by General Chemical Corp., Parsippany, N.J.) was added to the lagoon via a hose dispensing near the propeller as agitation continued. This addition of $AlCl_3$ equated to a 1% v/v rate, based on the estimated volume of material in the lagoon. Agitation continued for 1 hr prior to removal from the lagoon. Approximately 1600 L of treated waste was collected by taking a 57 L sample from every fifth 13,249 L "honey wagon" load. The treated and untreated manure samples were transported to the University of Arkansas Agricultural Experiment Station in Fayetteville, AR for rainfall simulation studies.

Runoff studies were conducted on 24 small plots (1.52 × 6.10 m) cropped to tall fescue (*Festuca arundinacea*) on a Captina silt loam soil (fine-silty, siliceous, mesic Typic Fragiudult). Complete details of the plot layout and construction can be found in DeLaune et al. (2004). Composite soil samples consisting of five random cores were taken for Mehlich-III P (0-15 cm). Mehlich-III P extracts were analyzed using ICP after extracting 2 g of soil with 14 mL of Mehlich-III solution for 5 min and filtered through a Whatman (Maidstone, UK) no. 1 filter (Mehlich, 1984). Mean Mehlich-III soil P concentrations for each block of plots were not significantly different (table 1).

The experimental design was a randomized complete block design with six replications of four treatments, consisting of 1) untreated swine manure, 2) swine manure treated with $AlCl_3$ *in situ*, 3) swine manure treated with $AlCl_3$ post collection, and 4) swine manure treated with $AlCl_3$ and agricultural lime ($CaCO_3$) post collection. All treatments were applied at a total P rate equivalent to 112 kg ha^{-1} (100 lb acre^{-1}). Post collection treatments were applied to the previously collected untreated manure immediately prior to application to runoff plots. Before adding amendments to post collection treatments, the untreated manure was homogenized by pumping. For each plot, 18.9 L of untreated manure was pumped into a container for treatment with amendments. For the $AlCl_3$ post treatment, 200 mL of $AlCl_3$ (≈1% v/v) was added and thoroughly mixed. For the $AlCl_3$/lime post treatment, 200 mL of $AlCl_3$ (≈1% v/v) and 30 g of lime ($CaCO_3$; ≈0.15% m/v) were added and thoroughly mixed. These rates were determined after experimenting with different rates within the laboratory. Each treatment was uniformly applied to each plot.

Table 1. Selected properties of manure applied and soil test P of rainfall simulation plots.

	n	Soluble P (mg L^{-1})	Soluble P Applied (kg ha^{-1})	pH	EC	Mehlich III Soil Test P (mg kg^{-1})
Untreated Control	6	146.2a	2.66a	7.76a	6.86b	285.6
$AlCl_3$ post	6	98.4b	1.79b	6.77c	15.48a	289.4
$AlCl_3$ *in-situ*	6	86.0c	1.56c	6.82c	15.78a	336.4
$AlCl_3$ + lime	6	45.2d	0.82d	7.04b	15.97a	256.1
LSD (0.05)		5.05	0.09	0.09	1.42	NS

A 250-mL subsample of manure applied to each plot was taken for analysis of soluble reactive P (SRP) and total P. Swine manure was collected in 250-mL centrifuge tubes *in situ* and placed directly on a mechanical shaker upon return to the laboratory. The sample was then centrifuged at 8,000 RPM for 20 min and filtered through a 0.45-µm membrane and acidified to pH 2 with HCl for SRP analysis. Soluble reactive P was determined colorimetrically using the automated ascorbic reduction method (APHA, 2005). Total P was determined using inductively coupled argon plasma spectrometry (ICAP) after digesting with nitric acid (Zarcinas et al., 1987).

Rainfall simulators were used to provide a 5 cm h^{-1} storm event sufficient in length to cause 30 min of continuous runoff 1, 8, 15, 17, and 24 days after application. Runoff samples were collected at 2.5, 7.5, 12.5, 17.5, 22.5, and 27.5 minutes after initial runoff. The six samples from each plot were composited based on flow rates at the time of sampling. Composited runoff samples were filtered through a 0.45-µm membrane and acidified to pH 2 with concentrated HCl. Soluble reactive P concentrations in the runoff water were determined colorimetrically on the filtered, acidified samples using the automated ascorbic acid reduction method (APHA, 2005).

Rainfall simulations were conducted 1 week prior to any manure application to measure background P concentrations from the 24 runoff plots. There were no significant differences among treatment blocks. Background SRP concentrations in the runoff water were 1.82, 1.75, 1.59, and 1.40 mg L^{-1} for $AlCl_3$ *in-situ*, $AlCl_3$/lime, $AlCl_3$ post collection, and untreated manure treatments, respectively.

Analysis of variance was used to determine significant treatment effects (SAS Institute, 1990). When significance was indicated, means were separated using Fisher's protected LSD (P <0.05).

Results and Discussion

Manure Characteristics

Manure pH of the untreated manure was 7.76 (table 1). Additions of $AlCl_3$ significantly reduced the pH of the manure, with pH ranging from 6.77 to 7.04. This reduction in pH is expected due to hydrolysis by aluminum. This effect has been shown in both wet and dry manure systems, which results in reduced ammonia emissions when treatments are applied within the housing facility (Smith et al., 2004; Moore et al., 1995, 1996, 1999). Among $AlCl_3$ treatments, lime additions resulted in significantly higher manure pH. As may be expected, manure EC was significantly higher for all $AlCl_3$ treatments than the untreated control (table 1).

Total P of the manure averaged 5500 mg L^{-1} with a total solids content of 11%. As $AlCl_3$ reduces P solubility in the manure, total P is not affected by$AlCl_3$ additions. Smith et al. (2004) reported no effect of $AlCl_3$ additions, ranging from 0 to 0.75% (v/v), to swine manure pits within a nursery facility on manure total P concentrations. However, Al treatments can have a significant effect on total P removal if solids are separated after treatment (Timby et al., 2004).

Whereas total P concentrations are not affected by $AlCl_3$ additions, soluble P concentrations are significantly affected (table 1). The mean SRP concentration in the untreated manure applied was 146 mg P L^{-1} (table 1), which was significantly higher than all other treatments (table 1). Treating the lagoon with $AlCl_3$ *in-situ* significantly reduced manure SRP concentrations compared to the untreated control, reducing SRP concentrations by 41%. In comparison, manure treated with $AlCl_3$ post collection reduced manure SRP concentrations by 33% over the untreated control. Differences between the $AlCl_3$ treatments applied *in-situ* and post collection can likely be attributed to the fact that a 1% (v/v) rate was not achieved when treating *in-situ*. A higher rate of $AlCl_3$ could have been added to further reduce SRP concentrations in the manure without adverse effects, such as low pH. If excessive amounts of Al are added, SRP concentrations can increase at low pH due to re-solublized amorphous P (Timby et al., 2004). Other studies have shown that Al amendments to liquid manure systems decreased P concentrations in manure by as much as 90% (Smith et al., 2001; DeBusk et al., 2008). It has been reported that as the total solids concentration of manure increases, higher chemical dosages are needed to achieve P removal (Vanotti et al., 2002; Oh et al., 2005). Most of the studies evaluating the effect of chemical amendments on P removal from liquid systems have been conducted on flush systems which have much lower total solids content (<3%) than the system used in this study, which was a lagoon undergoing total cleanout (total solids = 11%). However, amending the untreated manure with $AlCl_3$/lime post collection did result in a 69% reduction of SRP concentrations, significantly lower than all other treatments (table 1).The addition of lime should increase solubilization and precipitation reactions.

Runoff Study

With time, the use of $AlCl_3$ appeared to have minimal effect on runoff pH and EC (table 2). Smith et al. (2004) also observed little effect in runoff pH from $AlCl_3$ amended swine effluent. The most pronounced differences were for the first runoff event after application, where all $AlCl_3$ treatments resulted in significantly lower runoff pH values compared to the untreated manure (table 2). Although statistical differences were observed among treatments for each runoff event, pH values were similar. Perhaps most importantly, although manure EC values were significantly higher for $AlCl_3$ amended manure, this trend was not observed in runoff water. No significant differences of EC in runoff occurred among treatments for runoff events occurring 15 and 17 days after application.

The mean SRP concentration from plots fertilized with the untreated manure was 29.7 mg P L^{-1} for the first runoff event occurring one day after application (fig. 1; table 2). *In-situ* treatment did not significantly reduce SRP concentrations in runoff water compared to the untreated control. However, concentrations of SRP in runoff water during the first runoff event were significantly lower from plots fertilized with manure treated with $AlCl_3$ post collection over the untreated control. Plots fertilized with $AlCl_3$/lime, which had the lowest manure P solubility, had the lowest P concentrations in runoff water one day after application. Concentrations of P in the runoff water decreased with time each subsequent runoff event (fig. 2). No significant differences in runoff P concentrations were seen among treatments 15 and 17 days

Table 2. Runoff characteristics from plots fertilized with swine manure (n=6).

	pH	EC (μs cm^{-1})	Soluble P (mg L^{-1})	Soluble P Loss (kg ha^{-1})
1 day after application				
Untreated control	8.14a[a]	513.7b	29.7a	3.31a
$AlCl_3$ post	7.80b	595.0ab	23.4bc	2.31b
$AlCl_3$ *in-situ*	7.71b	626.2a	26.2ab	2.12b
$AlCl_3$ + lime	7.72b	526.8b	21.2c	2.16b
LSD (0.05)	0.14	82.0	3.90	0.88
8 days after application				
Untreated control	7.81a	372.0a	19.5a	2.00a
$AlCl_3$ post	7.66bc	366.0ab	17.0ab	1.69ab
$AlCl_3$ *in-situ*	7.60c	393.7a	20.4a	1.76ab
$AlCl_3$ + lime	7.74ab	347.0b	15.1b	1.21b
LSD (0.05)	0.10	35.2	3.88	0.70
15 days after application				
Untreated control	7.69a	259.8ab	12.7	2.13a
$AlCl_3$ post	7.66ab	257.0ab	11.6	1.89ab
$AlCl_3$ *in-situ*	7.59b	265.3a	12.3	1.98ab
$AlCl_3$ + lime	7.73a	254.0b	11.2	1.45b
LSD (0.05)	0.07	8.99	NS	0.54
17 days after application				
Untreated control	7.82a	254.8	10.57	1.77
$AlCl_3$ post	7.78b	254.0	10.0	1.55
$AlCl_3$ *in-situ*	7.69c	256.8	10.2	1.50
$AlCl_3$ + lime	7.81ab	254.5	9.6	1.37
LSD (0.05)	0.05	NS	NS	NS
24 days after application				
Untreated control	7.61a	263.2	8.29a	1.19a
$AlCl_3$ post	7.56a	255.2	6.54b	1.16a
$AlCl_3$ *in-situ*	7.45b	256.0	6.56b	0.86b
$AlCl_3$ + lime	7.62a	258.7	7.63ab	0.94ab
LSD (0.05)	0.11	NS	1.26	0.26

[a] Superscripts denotes differences during a particular sample day.

after application (table 2). As total P concentrations in runoff water were not measured, it can be expected that trends are similar between total P and SRP runoff since as much as 85% of the runoff P is SRP. This trend has been noted in several studies conducted at this location (Edwards and Daniel, 1993; Shreve et al., 1995; Smith et al., 2001, 2004; DeLaune et al., 2004, 2006).

Soluble reactive P loads (loss in kg ha^{-1}) for the first runoff event were significantly higher from plots fertilized with untreated manure than those fertilized with manure treated with $AlCl_3$ (table 2), including the *in-situ* treatment. For the first runoff event, plots fertilized with manure treated with $AlCl_3$ *in-situ* reduced SRP loads by 30% compared to the untreated manure. Applications of the untreated manure resulted in higher SRP loads for each of the five runoff events (table 2). The cumulative P loss from the five runoff events was highest from plots fertilized with the untreated manure (fig. 3). Treatment of manure with $AlCl_3$ *in-situ* reduced cumulative SRP losses by 26% compared to the untreated manure. Phosphorus losses in runoff water have been shown to be highly correlated with the solubility of the fertilizer source, with P losses in runoff water increasing as the levels of soluble P increase within the fertilizer source (Kleinman et al., 2002; DeLaune 2004; Smith et al., 2004). This general trend was also observed in this study as cumulative P losses for the five runoff events increased with increasing manure P solubility (fig. 4). This highlights the importance of manure P solubility in controlling concentrations of P in runoff. As total P application rates were equivalent for all manure treatments, manure SRP concentrations were affected by chemical amendments which subsequently affected SRP application rates and P losses in runoff water.

Conclusions

Aluminum chloride additions to swine manure reduced SRP concentrations in manure by as much as 69%. Data indicated that addition of $AlCl_3$ to swine lagoons *in-situ* during clean out can effectively reduce SRP levels in the manure by 41%. In comparison, equivalent $AlCl_3$ treatments mixed post collection reduced manure SRP concentrations by 33%, which may be attributed to a possible higher treatment dosage applied *in-situ* as rates were based on the estimated total volume of the lagoon. These reductions in manure SRP concentrations resulted in lower SRP land application rates. Although total P application rates were the same among treatments, runoff P concentrations and P loads differed due to differences in P solubility of the manure. This indicates the importance of the role in manure SRP levels in regulating the amount of P in runoff water. As SRP

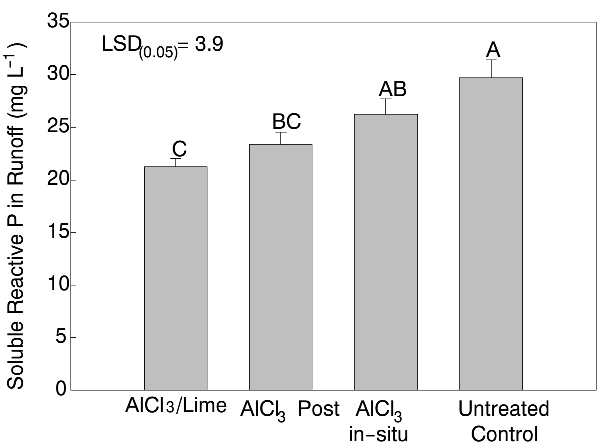

Figure 1. Concentrations of soluble reactive P in runoff water from plots fertilized with swine manure, treated and untreated, one day after application.

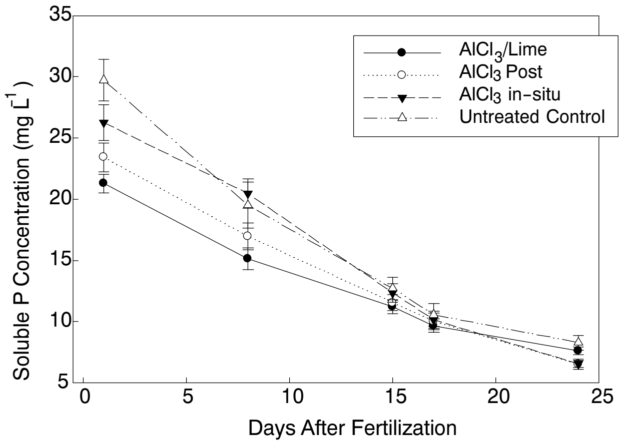

Figure 2. Concentrations of soluble reactive P in runoff water from fertilizer treatments during rainfall simulations that occurred between 1 and 24 days after fertilizer application.

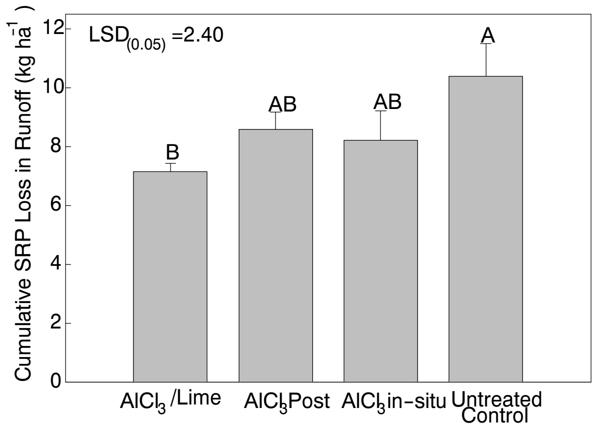

Figure 3. Cumulative soluble reactive P loss in runoff water from fertilizer treatments for five runoff events following application.

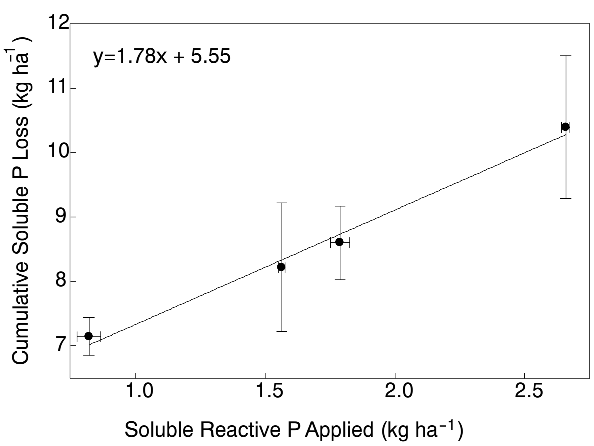

Figure 4. Relationship between cumulative soluble reactive P loss over five runoff events and the amount of soluble reactive P applied.

application rates increased, P loads from runoff plots also increased. *In-situ* $AlCl_3$ treatment of the swine lagoon resulted in a 26% reduction in cumulative P loads compared to plots fertilized with untreated manure.

Results from this study show that $AlCl_3$ can successfully be applied during lagoon cleanout to control SRP concentrations in manure and subsequently reduce P runoff. Producers should consider using chemical amendments in-house to potentially gain the most economical and environmental benefit. Such treatment can significantly reduce ammonia emissions while reducing SRP levels in the manure. However, in cases where lagoons have not undergone complete lagoon cleanout for some time or have received untreated effluent, this relatively simple approach is a viable option. This is especially true for areas under strict P application guidelines or in watersheds with implemented TMDL's. Research is warranted to determine the long-term effects of $AlCl_3$ treatment on P buildup and solubility after land application.

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